

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 579 281 A1**

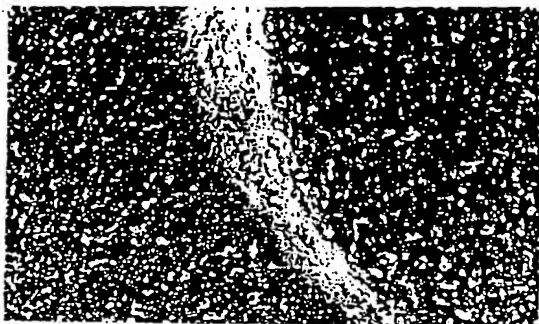
(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **93115376.1**(51) Int. Cl.<sup>5</sup>: **C09K 3/14**(22) Date of filing: **09.10.89**

This application was filed on 23 - 09 - 1993 as a  
divisional application to the application  
mentioned under INID code 60.

**St. Paul, Minnesota 55133-3427(US)**(30) Priority: **14.10.88 US 258196**(72) Inventor: **Wald, Vernon M., c/o Minnesota  
Mining and**(43) Date of publication of application:  
**19.01.94 Bulletin 94/03****Manufacturing Company,  
2501 Hudson Road**(60) Publication number of the earlier application in  
accordance with Art.76 EPC: **0 364 195****St. Paul, Minnesota 55144-1000(US)**(84) Designated Contracting States:  
**CH DE ES FR GB IT LI****Inventor: Kirk, Robert S., c/o Minnesota**(71) Applicant: **MINNESOTA MINING AND  
MANUFACTURING COMPANY  
3M Center,  
P.O. Box 33427****Mining and  
Manufacturing Company,  
2501 Hudson Road****St. Paul, Minnesota 55144-1000(US)**(74) Representative: **Baillie, Iain Cameron et al  
c/o Ladas & Parry  
Althelmer Eck 2  
D-80331 München (DE)**(54) **A grinding wheel.**

(57) Sintered ceramic abrasive grains having increased surface area are incorporated into improved "shelling-resistant" grinding wheels. The grinding wheels comprise a vitreous bond and abrasive grains in which a portion of said abrasive grains are alumina based ceramic particles made by a sol-gel process. These alumina based ceramic abrasive grains are made by providing first particles comprising alpha-alumina precursor, introducing fine particles which can be sintered directly to the surface of the first particles upon sintering of the same, and heating the mixture of particles under sintering conditions to cause autogenous bonding of the fine particles to the surface of each of the first particles.

**FIG.1**

Technical Field

This invention relates to grinding wheels containing shelling-resistant ceramic abrasive grain.

5 Background Art

Shelling is a term sometimes employed by those familiar with the abrasive industry, particularly the coated abrasive industry, which refers to the phenomenon whereby abrasive grains are released prematurely from a bond system which is typically intended to hold the abrasive grain throughout the useful life of the abrasive grains. The term "shelling" may have been adopted because someone thought the phenomenon of the abrasive grains being released from the bond system was similar to the releasing of kernels of corn from an ear of corn during a corn shelling operation. While there are some exceptions, e.g., where the abrasive product is used as a source of abrasive grain for a slurry, shelling of abrasive grain from abrasive products is unwanted because it has the effect of reducing the efficiency of the abrasive product because of the loss of the abrading surfaces which would have been provided by the missing abrasive grain, and for other reasons explained below. The decreased efficiency by shelling can be noted in all types of abrasive products such as banded abrasive products, e.g., grinding wheels, and non-woven abrasive products, but is particularly notable in coated abrasive products where substantially all of the abrasive grains are held on a sheet by the bond system with one end of each grain typically being exposed or nearly exposed. The loss of abrasive grain by shelling from coated abrasive products can provide non-abrasive areas on the coated abrasive surface, reducing abrasive efficiency and possibly resulting in uneven surface finishing.

The shelling problem can be particularly significant when the abrasive product is used for high stock removal applications. During such use, the abrasive product must be able to withstand high pressures and rotative speeds and still provide sufficient abrasive cut. For example, a coated abrasive disc can traverse 12,000 revolutions per minute (rpm) and be subjected to an interface pressure as high as 15 kg/cm<sup>2</sup>. While these severe conditions are preferred because they usually result in increased cut rates, they also severely tax the adhesive bond between the abrasive grain and the bond system. If this bond fails, abrasive grains are ejected (or shelled) from the coated abrasive product at an extremely high rate of speed which could result in serious injury to the operator, particularly when the abrasive grains are of a large grit size. This hazard is of grave concern to those in the abrasives industry and it sometimes results in products not being used to their full potential because of the possible safety hazard.

Furthermore, many abrasive products, particularly coated abrasive products, utilize moisture-susceptible resinous bond systems, the most popular comprising phenolic resin. Bond systems based upon phenolic resins are known to increase the potential for an abrasive product to shell as the moisture level of the grinding conditions is increased.

Many solutions to the shelling problem have been proposed, but they have been either impractical, expensive, of little utility, or not particularly suited for use with sintered ceramic abrasive grains.

The earliest known reference specifically directed to solving the shelling problem is U.S. Patent No. 1,528,543 (Hartmann) which discloses a process for treating the surfaces of crystalline mineral materials to scratch and roughen the grain surfaces and thus increase their bonding qualities. Various other references disclose the adhesion of smaller particles to the surface of larger particles to increase surface area by utilization of a bonding layer or flux to obtain particles having surface bonded smaller particulate material. For example, U.S. Patent No. 3,269,815 (Koopman) discloses coating abrasive grain with finely divided particles of solid material such as carbides and nitrides by cementing these particles to the abrasive grain by a thin ceramic film such as glass. The thin ceramic film will soften at a temperature less than the softening or melting of the abrasive grain or the solid materials to thereby cement the finely divided particles to the abrasive grain to promote resin adherence and increase the bonded strength between the particles of abrasive grain when in a bonded abrasive article. Additionally, U.S. Patent No. 4,472,173 (Bruning et al) discloses corundum abrasive grain which is coated with ground frit, a binder and fine grain highly abrasive material for the purpose of improving adhesion of the abrasive grain in its processing to resin-bonded abrasives.

Additionally, certain references disclose forming compacts of smaller particles which would inherently have a greater surface roughness. For example, U.S. Patent No. 4,252,544 (Takahashi) discloses alumina abrasive grain constructed of electro-fused or high temperature calcined alumina coarse crystal particles and alumina fine crystal particles which are located between the alumina coarse crystal particles. These abrasive grains are manufactured by forming alumina coarse powder of a particular type, forming alumina fine powder of a particular type, kneading the alumina coarse powder and alumina fine powder in the presence of water or, if necessary, primary binder, extruding the kneaded material by means of a

mechanical extruder, drying the extruded material, cutting the extruded material to a predetermined length, and sintering the dried and cut pieces of the extruded material at a temperature higher than that of the calcining temperature of the fine powdered alumina and lower than 1700°C.

There is no indication in any of the aforementioned references that the teachings could be utilized to produce alpha-alumina based ceramic abrasive grain having desirable physical properties without altering the same and without modifying the ceramic abrasive grains by the application or binder layers or flux. The type of ceramic abrasive grain desired to be improved according to the present invention is, for example, that disclosed in assignee's U.S. Patent No. 4,744,802 (Schwabel). Other references which disclose the preparation of alumina-based ceramic abrasive grain of this type include U.S. Patent Nos. 4,314,827 (Leitheiser et al), 4,518,397 (Leitheiser et al) and 4,574,003 (Gerk).

None of the above mentioned references discloses ceramic particulate material having inorganic material autogenously bonded to the surface thereof to provide an improved abrasive grain which is shelling resistant, or abrasive products such as bonded abrasive products, which contain the same.

## 15 Summary of the Invention

According to one aspect of the present invention, grinding wheels comprising a vitreous bond and abrasive grains in which at least a portion of said grains are alumina based ceramic particles made by a sol-gel process are provided. The improved abrasive grains comprising ceramic particulate material have inorganic material autogenously bonded to the surface thereof. The term "autogenously bonded" means that separated surface masses are bonded to the surface or each ceramic particle without any type of external bonding medium such as flux, vitreous bonding material, organic binder, glass, or the like. Bonding of the surface particulate materials is solely as a result of binder-free adhesion between the precursor of the material forming the abrasive grain and the precursor of the material forming the inorganic mass which ultimately forms a permanent bond therebetween on firing to sinter the precursor materials to form a ceramic material.

From another aspect of the invention there is provided a grinding wheel comprising abrasive grains and a vitreous bond wherein the abrasive grains are ceramic particles each of which is coated with inorganic material to provide a surface area ratio of at least 1.5 as compared to the grain before coating.

It has been discovered, quite unexpectedly, that inorganic surfaces may be formed on ceramic abrasive grains during the sintering operation without deleterious effect of the abrading properties of the resultant abrasive grain.

There is disclosed a method of making ceramic abrasive grain each grain of which is characterized by having autogenously bonded to the surface thereof inorganic material. The method comprises the steps of providing first particles comprising alpha-alumina precursor material, each particle of which is sinterable to alpha-alumina-based abrasive grain, introducing second particles much finer than the first particles, the second particles being capable of autogenous bonding to the surface of the first particles upon sintering of the first particles to a hard of inorganic material, and heating the particles under sintering conditions to sinter the first particles and cause autogenous bonding of the second particles to the surface of each of the first particles.

The process contemplates introducing the second particles by tumbling the first particles to cause the first particles to wear away on their surfaces to generate the second particles. This is done without substantially affecting the particle size of the first particles. The tumbling is continued until attachment of the generated second particles to the surface of each of the first particles results. The method also contemplates the introduction by addition of second particles to the first particles of second particles which are of a material which is different from the composition of the material forming the first particles. The second particles are then tumbled with the first particles to cause the second particles to attach to the surface of the first particles.

For at least a portion of the grains the method involves preparing the first particles by providing a mixture of an aqueous dispersion of alumina-hydrate, gelling the mixture, drying the gelled mixture to produce a dried solid, and crushing the dried solid to produce the first particles.

The method may include the step of calcining at least the first particles to substantially remove bound volatile materials prior to introducing the second particles into the mass of first particles.

As previously stated, at least some of the abrasive grains of the invention comprise alpha-alumina based ceramic particles having autogenously bonded inorganic material to provide a multiplicity of surfaces on each abrasive grain. The preferred abrasive grain according to the invention has surfaces which comprise a material selected from the group consisting of alumina, alpha alumina, alumina:zirconia, zirconia, silicon nitride, rare earth metal oxides, yttria, chromia, ceria, titanium carbide, titanium nitride, silicon

alumina oxynitride, silicon aluminum oxycarbide, yttrium alumina-garnet, hexagonal rare earth aluminate, aluminum oxynitride, oxides of zinc, magnesium or nickel and mixtures thereof.

The abrasive grain according to the present invention also contemplates the inclusion of at least one modifying additive in the alpha-alumina based ceramic. The modifying additive preferably is an oxide of one or more metals selected from the group consisting of magnesium, zinc, zirconium, hafnium, cobalt, nickel, yttrium, praseodymium, samarium, ytterbium, neodymium, lanthanum, gadolinium, cerium, dysprosium, and erbium.

As mentioned, the invention provides specified abrasive products made with these abrasive grains. The abrasive products are in the form of bonded abrasive products, i.e. grinding wheels, which include a vitreous binder.

The ceramic abrasive grains according to the invention have increased surface area which results in improved adhesion to the bond system in abrasive type products. By improving the adhesion, the abrasive products can be utilized at higher pressures, which results in an increase in the stock removal rates. Additionally, abrasive products containing the abrasive grain of the invention will abrade significantly more stock from a workpiece than a corresponding abrasive product made without surface modification of the abrasive grain as herein described.

#### Brief Description of the Drawing

The invention may be further understood by reference to the Drawing wherein:

Fig. 1 is a 700x photomicrograph of the surface of an abrasive grain according to the present invention, photographed using a scanning electron microscope; and

Fig. 2 is a 700x photomicrograph of the surface of commercially available ceramic abrasive grain of the same composition of the grain of Fig. 1 except without surface modification according to the present invention.

#### Detailed Description

This invention pertains to alpha-alumina based ceramic abrasive grains which are prepared by drying and firing particulate precursor material below the melting temperature of the ceramic to achieve sintering of the dehydrated starting materials. During heating the precursor material will be transformed to a dehydrated metal oxide structure which will densify as heating continues. The most common alpha-alumina-based ceramic may be modified with oxides of metals such as magnesium, nickel, zinc, yttria, rare earth oxides, zirconia, hafnium, chromium or the like. The preferred method of making the ceramic abrasive grain is by the so called sol-gel process disclosed in the following U.S. Patents: 4,314,827; 4,518,397; 4,574,003; 4,623,364; and 4,744,802.

To prepare the sol gel alumina-based ceramic abrasive grains, a dispersion comprising from about 2 to almost 60 weight percent alpha alumina oxide monohydrate (e.g., boehmite) is first formed. The boehmite can either be prepared from various techniques well known in the art or can be acquired commercially from a number of suppliers. Examples of commercially available materials include Disperal™, produced by Condea Chemie, GMBH and Catapal™, produced by Vista Chemical Company. These aluminum oxide monohydrates are in the alpha-form, are relatively pure (including relatively little, if any, hydrate phases other than monohydrate), and have a high surface area.

The dispersion may contain a precursor of a modifying additive which can be added to enhance some desirable property of the finished product or increase the effectiveness of the sintering step. These additives are in the form of soluble salts, typically water soluble, and typically consist of a metal-containing compound and can be a precursor of the oxides of magnesium, zinc, cobalt, nickel, zirconium, hafnium, chromium, titanium, yttrium, rare earth oxides, and mixtures thereof. The exact proportions of these components that are present in the dispersion are not critical to this invention and thus can vary to convenience.

A peptizing agent is usually added to the boehmite dispersion to produce a more stable hydrosol or colloidal dispersion. Monoprotic acids or acid compounds which may be used as the peptizing agent include acetic, hydrochloric, formic and nitric acid. Nitric acid is a preferred peptizing agent. Multiprotic acids are normally avoided since they rapidly gel the dispersion making it difficult to handle or mix in additional components. Some commercial sources of boehmite contain an acid titer (such as absorbed formic or nitric acid) to assist in forming a stable dispersion.

The dispersion can be formed by any suitable means which may simply be the mixing of aluminum oxide monohydrate with water containing a peptizing agent or by forming an aluminum oxide monohydrate

slurry to which the peptizing acid is added. Once the dispersion is formed, it is then gelled. The gel can be formed by any conventional technique such as the addition of a dissolved or dispersed metal containing modifying additive, e.g., magnesium nitrate, the removal of water from the dispersion of some combination of such techniques.

The dispersion may contain a nucleating agent to enhance the transformation to alpha alumina. Suitable nucleating agents include fine particles of alpha alumina, alpha ferric oxide or its precursor and any other material which will nucleate the transformation. The amount of nucleating agent is sufficient to effect nucleation. Nucleating such dispersions is disclosed in assignee's U.S. Patent No. 4,744,802.

Once the gel has formed it may be shaped by any convenient method such as pressing, molding, coating or extrusion and then carefully dried to produce a dried solid material.

The gel can be extruded or simply spread out to any convenient shape and dried, typically at a temperature below the frothing temperature of the gel. Any of several dewatering methods, including solvent extraction, can be used to remove the free water of the gel to form the solid.

After the gel is dried, the dried solid can be crushed or broken by any suitable means, such as a hammer or ball mill or a roll crusher, to form abrasive grain precursor particles hereafter referred to as precursor particles. Any method for comminuting the solid can be used and the term "crushing" is used to include all such methods.

The ceramic abrasive grain of the invention with increased surface area may be prepared by tumbling the non-sintered particles. Non-sintered particles refer to particles that have been dried but not fully sintered, typically having a density which is less than 60%, of theoretical density in such a condition. Calcined non-sintered particles are typically about 50% of theoretical density. The preferred method of making the non-sintered particles is disclosed in U.S. Patent No. 4,744,802 assigned to the assignee of the present application. Tumbling of the non-sintered particles may be accomplished either prior to calcining or prior to final firing (sintering). The non-sintered particles are relatively soft and, when they tumble together in a mixer, the edges break off to produce fines which are redeposited upon the surface of the abrasive grains via mechanical impingement as tumbling is continued. In a first embodiment the non-sintered particles are tumbled in a mixer to generate fine particulate material. Tumbling may be accomplished by charging a mixer with a specified amount of non-sintered particles. At this point in the process, the non-sintered particle will be relatively soft. Tumbling results in contact between non-sintered particles which generates fine particles. Continued tumbling causes the fines to redeposit on the surfaces of the non-sintered particles via mechanical impingement. During final firing, the fine particles sinter along with the non-sintered particle to form abrasive grains. The redeposited fine particles form on the surface of the abrasive grain, thereby increasing the surface area of the abrasive grain which results in improved adhesion to the bond system.

In a second embodiment, the non-sintered particles are tumbled in a mixer with added fine particles which are of a different composition from that of the non-sintered particles yet which form inorganic surfaces on the abrasive grains. These fines, along with the fines of the non-sintered particles that are broken from the surface of the non-sintered particles during the tumbling, are redeposited onto the surface of the non-sintered particles during continued tumbling. Final sintering causes the fine particles, both the added and the generated, to sinter along with non-sintered particles to form abrasive grain having inorganic surfaces.

In order to facilitate the tumbling, non-sintered particles are charged to a mixer in a specified weight ratio. In general, the mixer should be about 10 to 75% full, preferably about 20 to 50% full by volume with non-sintered particles. The non-sintered particles are tumbled for a time sufficient to generate an adequate amount of fine particles without undesirably rounding the edges of the non-sintered particles and thereby on sintering producing an abrasive grain which has undesirably rounded edges which does not abrade as well as an abrasive with sharp edges. Some experimentation may be needed to predict the exact time necessary to tumble the non-sintered particles, since the time is a function of the energy generated. Non-sintered particles which have been pre-fired or calcined require more tumbling time, since the particles are harder than non-calcined particles. The tumbling times may easily be determined by those skilled in the art. In general, the more energy generated for a given time period, the less tumbling time required. This energy is the mechanical energy generated by the non-sintered particles interacting with one another but is also a function of the mixer design. It is also preferred to use a mixer with baffles or flanges to increase the generated energy and thus reduce the tumbling time. Although any type of mixer may be utilized, a closed system is preferred to avoid fine particle loss. Not all mixer designs will provide the necessary conditions to cause the fine particles to adhere to the non-sintered particles via mechanical impingement. For example, a vibratory mill does not provide the necessary interactions between the particles to cause the fines to break off and deposit themselves on the unsintered particles. The preferred mixer design is a ball mill without the

abrasive media. Typical tumbling times are on the order of 5 to 180 minutes, preferably 20 to 50 minutes.

In the first embodiment, the non-sintered particles alone are tumbled to produce fines of the same chemical composition as the non-sintered particles. In the second embodiment, the non-sintered particles are tumbled with added fines of a different composition, resulting in a blend of these with fines of the same chemical composition which are generated as the non-sintered particles are tumbled. The second embodiment has an unexpected benefit in that it permits the tailor-making of abrasive grain surfaces by selecting the appropriate fine particles to be tumbled with the non-sintered particles, it being well known in the art that the surface of the abrasive grain has a significant role during abrading applications.

After crushing (and tumbling if done at this time), the dried gel particles are then calcined to remove essentially all volatiles and transform the various components of the grains into ceramics. The dried gel particles are generally heated (calcined) at a temperature between about 400 °C and about 800 °C and held within this temperature range until the free water and over 90 weight percent of any bound water is removed.

Tumbling can occur either before or after the calcining step so long as it occurs before the final firing step. It is preferred that the tumbling be done before the calcining step for ease of handling.

The calcined particles are then sintered by heating to a temperature of between about 1000 °C and about 1650 °C and holding within this temperature range until substantially all of the alpha alumina precursor material (e.g., alpha alumina monohydrate) is converted to alpha alumina. Of course, the length of time to which the ceramic must be exposed to the sintering temperature to achieve this level of conversion and will depend upon various factors but usually from about 5 to about 30 minutes is sufficient.

Other steps can be included in this process, such as rapidly heating the material from the calcining temperature to the sintering temperature, sizing granular material, centrifuging the dispersion to remove sludge waste, etc. Moreover, this process can be modified by combining two or more of the individually described steps, if desired.

It is conceivable that a ceramic abrasive grain may go through several high temperature firing cycles. The tumbling must be done prior to the last or sintering firing cycle. The tumbling process should not be accomplished after sintering, since it would cause small parts of the abrasive grains to break off with no means to sinter them onto the abrasive grain surface.

Fig. 1 shows the protuberant surface of an abrasive grain according to the invention while Fig. 2 by contrast shows the very smooth surface of a conventional ceramic abrasive grain. It should be noted that the increased surface area of the abrasive grain of the invention does not result because of an increase of porosity of the abrasive grain. The abrasive grain of the invention preferably has a density of at least 90% of theoretical. While porous abrasive grains tend to have a large surface area, their performance is substantially inferior because of decreased strength and integrity.

The surface area ratio is one means by which the abrasive grain of the invention may be characterized. The abrasive grain of the invention has a surface area ratio of at least 1.5, preferably at least 2.0. Surface area ratio, a measure of the increase in surface area of the abrasive grain, is determined by dividing the surface area of the abrasive grain of the invention by the surface area of the standard untreated graded abrasive grains for a given grade. The surface area ratio is a more meaningful way to characterize the increase in surface area since every abrasive grain grade has a different particle size and would thus have a different surface area. The grading standard for abrasive grains may be found in American National Standard Institute (ANSI) Standard No. B74.18, 1984; the coarse and control fractions were used for a given grade to calculate surface area ratios. Untreated graded standard abrasive grains may be purchased from Minnesota Mining and Manufacturing (3M) Company of St. Paul, Minnesota, under the trade designation Cubitron abrasive grain. The tumbled abrasive grains were made according to the teachings in U.S. Patent No. 4,744,802, except that the abrasive grains were tumbled for 20 minutes in a ball mill containing no grinding or abrasive media prior to pre-firing. The ball mill was approximately 1.82 meter in length with a 1.82 meter inside diameter and was rotated at 16 rpm. Baffles (5.1 cm high and 5.1 cm thick) were spaced around the inside circumference of the ball mill at approximately 46 cm intervals. The remainder of the steps were the same as the teachings of U.S. Pat. No. 4,744,802.

Listed below are the surface areas of the untreated ANSI Standard graded abrasive grain and the tumbled abrasive grain made according to the invention and the calculated surface area ratio. The surface area was measured on a Quantosorb, Model QS 13 surface area measuring device which was obtained from Quantachrome Company, Syosset, New York. The samples were soaked in nitrogen gas for 20 minutes prior to testing.



Surface Area Measurements			
Grade	ANSI Grains (m <sup>2</sup> /g)	Tumbled Grains (m <sup>2</sup> /g)	Ratio
36	0.045	0.26	5.8
50	0.041	0.29	7.1
80	0.19	0.40	2.1
120	0.12	0.47	3.8

The coating on the surface of the abrasive grain resulting from attachment thereto of the fines is discontinuous, leaving exposed portions of the original surface of abrasive grain with an irregular coating of the fine inorganic particles. This discontinuous coating has greater surface area than a continuous coating, leading to improved adhesion to the bond system.

The materials from which the fine particles are chosen are sinterable to form a ceramic typically based on metal oxide, nitride, carbide, oxynitride, or oxycarbide. Examples of typical addition fines will sinter to the following: alumina, aluminum oxynitride, metal oxides of zinc, magnesium or nickel, alpha alumina, alumina zirconia, zirconia oxide, silicon nitride, rare earth oxides, yttrium oxide, cerium oxide, titanium carbide, titanium nitride, silicon alumina oxynitride, silicon aluminum oxycarbide, yttrium alumina-garnet, and hexagonal rare earth aluminates. The addition fines may be added as a precursor of the final sintered composition. The addition fines are preferably added directly to the mixer in a ratio from 1 part fines to 99 parts precursor particles to 30 parts fines to 70 parts precursor particles. The addition fines can be added to the mixer in a powder form. It has been verified via a scanning electron microscope and Energy Dispersion X-ray Analysis (EDAX) which determines elemental analysis that the addition fines are indeed attached to the surface of the abrasive grain.

Some addition fines may also co-react with the alumina-based abrasive grain during sintering. For example, the oxides of cobalt, nickel, zinc and magnesium will typically form a spinel structure with the alumina. Yttria will typically react with alumina to form  $3Y_2O_3 \cdot 5Al_2O_3$ , a garnet crystal phase. Praseodymium, samarium, ytterbium, neodymium, lanthanum gadolinium, cerium, dysprosium, erbium, and mixtures of two or more of these rare earth metals will typically react with alumina to form a garnet, beta alumina, perovskite, or hexagonal rare earth aluminate crystal structure.

The average particle size of the fines should initially be between about 0.05 and 50 micrometers. The average particle size of the non-sintered particle is between 50 micrometers to 1200 micrometers. In general, the large particle size fines do not work as well as the small particle fines on the small particle size non-sintered particles. For example, an abrasive grain having a particle size of 120 micrometers, typically would have fines on the order of 0.2 to 5 micrometers. Likewise, an abrasive grain having a particle size of 600 micrometers, preferably has fines on the order of 0.2 to 10 micrometers. The preferred addition fine average particle size is between 0.1 and 15 micrometers. If the particle size of the fines is too large, adhesion to the surface of the abrasive grain may be inadequate. If the particle size of the fines is too small, there would be little or no increase in surface area.

As mentioned, the ceramic abrasive grains of the present invention are conveniently handled and incorporated into bonded abrasive products. The methods of making such abrasive products are well known to those skilled in the art.

Bonded abrasive products typically consist of a shaped mass in the form of a grinding wheel. The vitrified binders used are curable at temperatures and under conditions which will not adversely affect the ceramic abrasive grains of the present invention.

A coupling agent is preferably present in the bond system. Typical examples of coupling agents and their useful quantities in abrasive products may be found in assignee's U.S. patent application Serial No. 132,485, filed December 14, 1987.

## Examples

The following non-limiting examples will further illustrate the invention.

### Control Example and Reference Examples 1-3

The Control Example and Reference Examples 1-3 compare the effect of tumbling on the performance of abrasive grain.

Control Example and Examples 1-3

The Control Example and Examples 1-3 compare the effect of tumbling on the performance of abrasive grain.

Control Example

The Control Example is abrasive grain made in a conventional way without tumbling with fines.

The Control Example grain was made according to the following procedure. Into a continuous mixer were charged 12,000 ml of deionized water, 282.5 g of 11N analytical reagent grade nitric acid, 4780 g of alpha aluminum oxide monohydrate powder at 78% solids sold under the trade designation Disperal<sup>®</sup> and 761 grams of an alpha iron oxide precursor aqueous solution at 10% solids. The charge was dispersed until a homogeneous solution was obtained. The resulting dispersion and an aqueous solution of magnesium nitrate [Mg(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O] were metered through an in line mixer to form a gel in an amount to provide the following composition after the final firing: 93.5% alpha alumina, 4.5% MgO and 2% Fe<sub>2</sub>O<sub>3</sub>. The resulting gel was then dried in a forced air oven at 150 °C to a friable solid.

The resultant dried material was crushed using an impact hammer mill and a roll crusher.

The dried, screened, crushed gel was calcined by being fed into the end of a kiln which was a 23 cm diameter 4.3 meter long stainless steel tube having a 2.9 meter hot zone, the tube being inclined at 2.4 degrees with respect to the horizontal, and rotating at 7 rpm, to provide residence time therein of about 15 minutes. The calciner had a hot zone feed end temperature of 350 °C and exit end temperature of 800 °C. The fired product from the calciner was fed into a 1390 °C kiln which was a 10.1 cm diameter 1.53 meter long silicon carbide tube inclined at 4.4 degrees with respect to the horizontal and having a 76 cm hot zone, rotating at 10 rpm, to provide a residence time therein of about 3.8 minutes. The abrasive grain exited the kiln into room temperature air where it was collected in a metal container and allowed to cool to room temperature. The abrasive grain was a conventional grade 36 and had an average particle size of 700 micrometers.

Abrasive Disc Preparation

After the abrasive grain was made, it was utilized in a coated abrasive disc. The discs were prepared using conventional coated abrasive making procedures, conventional 0.76 mm vulcanized fiber backings and conventional calcium carbonate-filled phenolic make resin and conventional cryolite-filled phenolic size resin. The average make weight was 172 grams/square meter, the average size grain weight was 696 grams/square meter. The make resin was precured for 90 minutes at 88 °C and the size resin was precured for 90 minutes at 88 °C followed by a final cure of 100 °C for 10 hours. The coating was done using conventional techniques in a one-trip operation with curing in a forced air oven. The cured discs were first conventionally flexed to controllably break the hard bonding resins. The test results can be found in Table 1 for the Shelling Test and Table 2 for the Cut Test.

Shelling Test

The Shelling Test is designed to measure the time it takes for the abrasive grain to shell from a coated abrasive disc. The test equipment included 17.8 cm diameter test coated abrasive discs with a 2.22 cm mounting hole attached to a 16.5 cm diameter 1.57 mm thick hard phenolic backup pad which was in turn mounted on a 15.2 cm diameter steel flange. The test disc so supported was rotated counter-clockwise at 3550 rpm. The 1.8 mm peripheral edge of a 25 cm diameter 1010 carbon steel disc-shaped workpiece, deployed 18.5° from a position normal to the abrasive disc and rotated counter-clockwise at 2 rpm, was placed into contact with the abrasive face of the abrasive disc under a load of 2.9 kg. The test endpoint was 20 minutes or when the disc begins to shell, i.e., a substantial portion of its abrasive grain flies off of the disc, whichever occurred first. At the end of the test the workpiece was weighed to determine the amount of metal cut (abraded) from the workpiece. The discs were humidified for one week prior to testing at the humidity level specified in Table I or II below.

Cut Test

For the Cut Test, the 17.8 diameter disc with a 2.22 cm center hole was attached to an aluminum backup pad have a beveled edge and used to grind the face of a 2.5 cm by 18 cm 1018 mild steel workpiece.

The disc was driven at 5,500 rpm while the portion of the disc overlaying the beveled edge of the back up pad contacted the workpiece at 5.92 kg pressure generating a disc wear path of about 140 cm<sup>2</sup>. Each disc was used to grind a separate workpiece for one minute each for a total time of 12 minutes each or for sufficient one minute time segments until no more than 5 grams of metal were removed in any one minute grinding cut.

#### Reference Example 1

Reference Example 1 was made and tested in the same manner as the Control Example except the abrasive grain was tumbled prior to calcining. Approximately 1200 kilograms of the dried gel was charged to a ball mill containing no grinding or crushing media. The ball mill was approximately 1.82 meter in width and had a 1.82 meter inside diameter and rotated at 16 rpm. Baffles (5.1 cm high by 5.1 cm thick) were spaced at 46 cm intervals around the inside circumference of the ball mill. The non-sintered particles of dried gel were tumbled for 10 minutes. After tumbling, the remainder of the steps were the same as in the Control Example.

#### Reference Example 2

Reference Example 2 was prepared and tested in the same manner as Reference Example 1, except the tumbling time was 20 minutes.

Table I

(Shelling)			
Example	Total Cut (grams)	Time to Shell (minutes)	% Relative Humidity
Control	192	3.9	30
Ref 1	320	7.1	30
Ref 2	424	18	30
Control	132	2.8	45
Ref 1	280	6.5	45
Ref 2	287	12.4	45
Control	44	0.8	70
Ref 1	98	1.4	70
Ref 2	171	4.6	70

Table II

(Cut)		
Example	Total Cut (grams)	% Relative Humidity
Control	1149	30
Ref 1	1216	30
Ref 2	1202	30

From the above listed data, there was a dramatic improvement in performance on the Shelling Test, especially at high humidities, indicating improved adhesion between the bond system and the abrasive grains according to Reference Examples 1 and 2 over that of the Control Example. The Cut Test results, where adhesion between the bond system and the abrasive grains is not as critical, showed a slight improvement in performance in Reference Examples 1 and 2 over the Control Example.

#### Reference Examples 3 through 5

Reference Examples 3 through 5 demonstrate the second embodiment of the invention in which added fine particles are tumbled with the precursor particles. The resulting abrasive grain had directly sintered to

its surface both the added fine particles and fine particles originating from the precursor particles.

### Reference Example 3

The abrasive grain and coated abrasive disc for Reference Example 3 was made and tested in the same manner as the Control Example except fines containing oxides of alumina and zirconia were tumbled with the abrasive grain precursor particles prior to calcining. The abrasive fines were made according to Example 1 of U.S. Patent No. 4,314,827. Approximately 5000 grams of the precursor particles of dried gel and 500 grams of fines containing oxides of alumina and zirconia were charged to a mixer. The fines were in the range 0.25 to 3 micrometers in size. The mixer had a volume of 1.15 cubic meters and was obtained from the Patterson- Keller Co. Inc., East Stroudsburg, as Model # P.K. 232213. The mixer did not have any baffles or flanges in its interior. The fines and the dried, screened, crushed gel precursor particles were tumbled for one hour. The remaining steps to produce the abrasive grain and the coated abrasive were the same as the Control Example. The test results can be found in Table III.

### Reference Example 4

The abrasive grain and coated abrasive disc for Reference Example 4 was made and tested in the same manner as Reference Example 4 except fine inorganic particles were abrasive fines containing oxides of alumina, yttria and magnesia, not alumina zirconia. The abrasive fines were made according to U.S. Patent 4,770,671 and contained 90% alpha alumina, 8.5% yttrium oxide and 1.5% magnesium oxide. During the final firing, the magnesium in the fines co-reacted with the alpha alumina in the grain to form a spinel. Also at the same time the yttria co-reacted with the alpha alumina to form  $3Y_2O_3 \cdot 5Al_2O_3$ .

### Reference Example 5

The abrasive grain and coated abrasive disc for Reference Example 5 was made and tested in the same manner as the Control Example except silicon nitride fines were tumbled with the abrasive grain precursor particles prior to calcining. Also, Reference Example 5 was subjected to different calcining and firing conditions necessary for the silicon nitride fines. After tumbling, the resulting coated precursor particles were packed into a 5 cm diameter, 30 cm long alumina tube which was placed into a 7.5 cm diameter stationary tube furnace where it was heated to a calcining temperature of 1050°C in a nitrogen atmosphere after which a 95% nitrogen/5% hydrogen atmosphere was maintained. The temperature was increased over several hours to 1350°C where it was held for 30 minutes to sinter the abrasive grain and then cooled over several hours to room temperature.

The abrasive grain was used to prepare abrasive discs which were tested as described above. Shelling Test results are shown in Table III.

Table III

(Shelling)			
Example	Total Cut (grams)	Time to Shell (minutes)	% Relative Humidity
Control	531	16	35
Ref 3	647	20	35
Ref 4	678	20	35
Ref 5	562	20	35
Control	208	5.2	70
Ref 3	396	12	70
Ref 4	378	12	70
Ref 5	355	12	70

It was very evident from the data shown in Table III that autogenously bonded added fines increased the adhesion between the abrasive grain and the bonding resin.

Reference Examples 6 and 7

Reference Examples 6 and 7 compare abrasive grain tumbled before and after calcining. The test results can be found in Table IV.

Reference Example 6

Reference Example 6 was made and tested in the same manner as Reference Example 1 except that a different ball mill was utilized to tumble the abrasive grain. Approximately 182 grams of the dried gel was charged into a ball mill containing no grinding or crushing media. The ball mill had an inside diameter of approximately 1.82 meter and a width of 0.3 meter. Baffles 5.1 cm high by 5.1 cm thick were spaced at approximately 46 cm intervals around the inside circumference of the ball mill. The ball mill rotated at 16 rpm. The non-sintered particles were tumbled for 20 minutes. After tumbling, the remainder of the steps were as in Reference Example 1. The non-sintered particles of Reference Example 6 were not calcined prior to tumbling.

Reference Example 7

Reference Example 7 was prepared and tested in the same manner as Reference Example 6, except the non-sintered particles were calcined prior to tumbling.

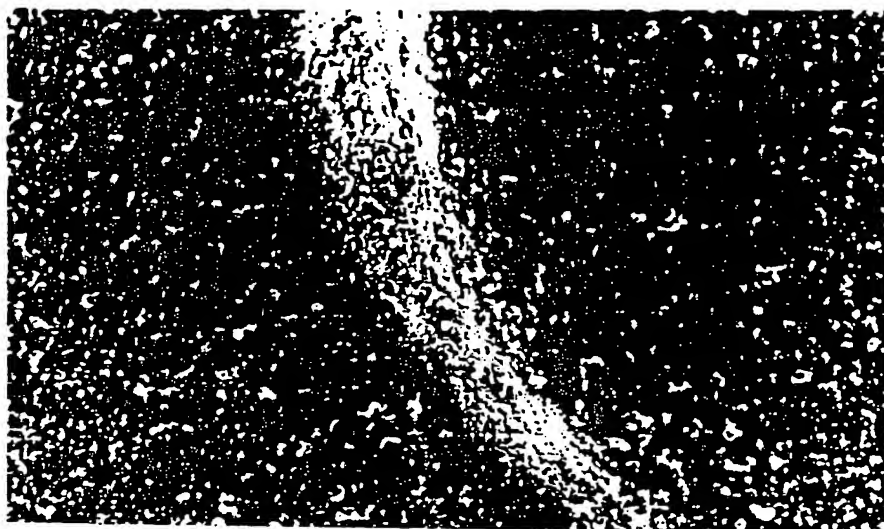
Table IV

Example Number	Total Cut (grams)	Time to Shell (minutes)	Calcined Before Tumbling	% Relative Humidity
Control	298	10	N/A	45
Ref 6	415	14	no	45
Ref 7	450	13	yes	45
Control	90	1.9	N/A	70
Ref 6	208	6.7	no	70
Ref 7	149	3.4	yes	70

It was concluded from the above data that tumbling either before or after calcining significantly improved the shelling resistance of the coated abrasive product.

**Claims**

1. A grinding wheel comprising a vitreous bond and abrasive grains in which at least a portion of said grains are alumina-based ceramic particles made by a sol-gel process each having a discontinuous coating of inorganic material autogenously bonded to the surface thereof.
2. A grinding wheel according to claim 1 wherein said abrasive grains are shaped.
3. A grinding wheel according to claim 2 wherein said shaped abrasive grains have been formed by extrusion.
4. A grinding wheel according to claim 2 wherein said shaped abrasive grains have been formed by moulding.
5. A grinding wheel comprising abrasive grains and a vitreous bond wherein the abrasive grains are ceramic particles each of which is coated with inorganic material to provide a surface area ratio of at least 1.5 as compared to the grain before coating.



*FIG. 1*



*FIG. 2*



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 5376

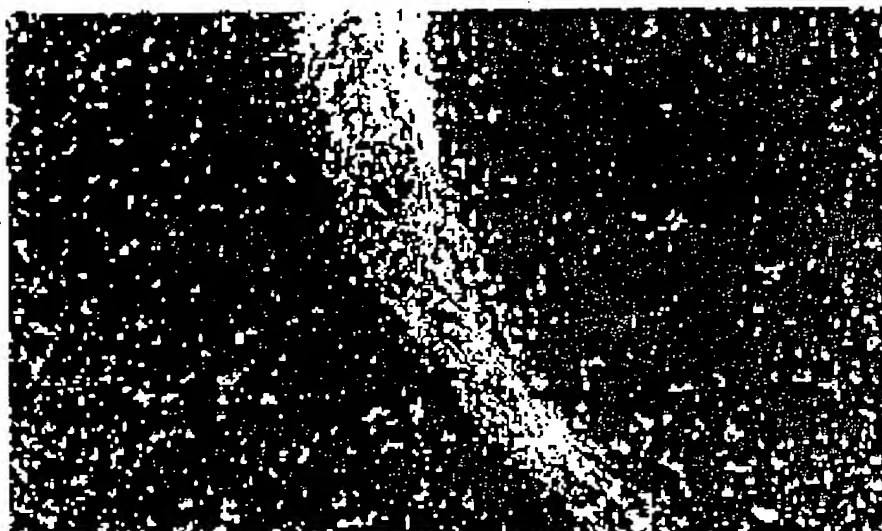
### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y,D	US-A-4 252 544 (TAKAHASHI) * column 3, line 34 - column 4, line 26; claims 1,2,8; example 1 * * column 8, line 29 - line 55 * ---	1-5	C09K3/14
Y	EP-A-0 209 084 (NORDDEUTSCHE SCHLEIFFMITTEL-INDUSTRIE CHRISTIANSEN ET ALL) * column 2, line 7-10; claims 1-10; example 1 * ---	1-5	
A,P	EP-A-0 294 208 (MINNESOTA MINING) * column 2, line 1 - line 32; claims 1,9 * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C09K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 November 1993	Examiner NICOLAS, H
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... A : member of the same patent family, corresponding document			

EPO FORM 1503 (11.92) (P04C01)

**THIS PAGE BLANK (USPTO)**





*FIG. 1*



*FIG. 2*

**THIS PAGE BLANK (USPT**